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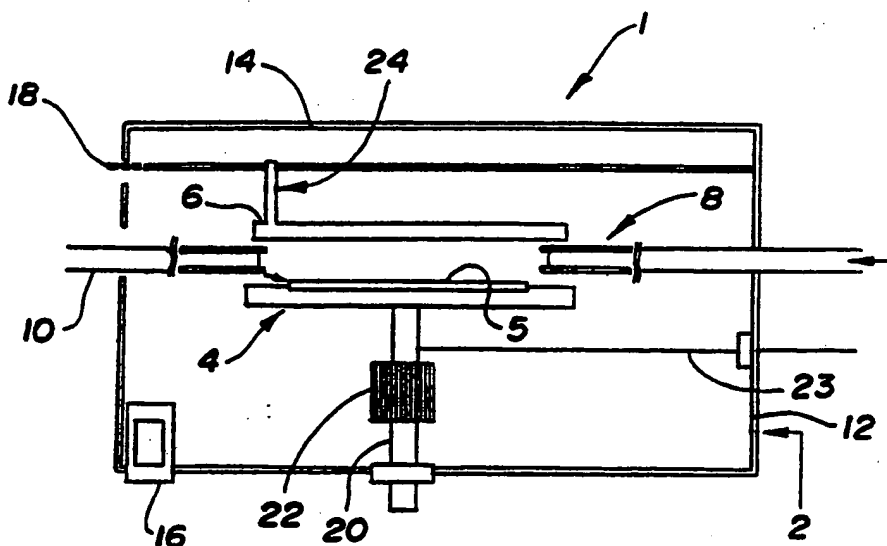
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(54) Title: METHODS AND APPARATUS FOR MATERIAL DEPOSITION

(57) Abstract

A method and apparatus (1) are disclosed for forming thin films of chemical compounds on substrates (5) in a vacuum chamber (2). The method includes steps of forming at least one stabilized solution of a desired chemical compound and a solvent, providing a substrate (5) within a vacuum deposition chamber (2), producing a mist of the stabilized solution using an ultrasonic device (46), and flowing the mist into the deposition chamber (2) in close proximity to the substrate using a unique nozzle device (8, 10) such that the mist deposits and forms a layer of the stabilized solution on the substrate (5).



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METHODS AND APPARATUS FOR MATERIAL DEPOSITION

Field of the Invention

5 The invention relates to methods for depositing high quality films of complex (compound) materials on substrates at high deposition rates, and apparatus for effecting such methods. Particularly, the invention relates to nonreactive chemical vapor deposition (CVD) methods and apparatus for depositing high quality, stoichiometrically-correct, thin films of a large variety of complex compounds at high deposition rates utilizing stabilized liquid compound
10 sources.

Description of Relevant Art

There are known methods for depositing thin films of complex compounds such as metal oxides, ferroelectrics, super-conductors, materials with high dielectric constants, gems, etc. Such known methods include: vacuum
15 evaporation (i.e., E-beam, laser ablation, etc.); vacuum sputtering (i.e., E-beam, D.C., R.F., ion-beam, etc.); powder metallurgy; reactive chemical vapor deposition; and liquid application methods (i.e., spin-on techniques, dipping and spraying). All of such known methods, however, have significant disadvantages associated therewith.

20 The present invention has been developed to overcome the many problems and disadvantages associated with known deposition techniques for depositing thin films of complex chemical compounds including those discussed above, and to generally fulfill a great need in the art by providing a production worthy process which can be used for easily and economically producing thin
25 films (from a few angstroms to microns in thickness) of various complex materials such as ferroelectrics, superconductors, and metal oxides.

Brief Description of the Drawings

Fig. 1 is a schematic view of a CVD apparatus according to a first embodiment of the invention.

30 Fig. 2 is an enlarged plan view of a nozzle assembly and an exhaust assembly used in the embodiment of Fig. 1.

Fig. 3 is an enlarged schematic view of a manifold system used in the first and second embodiments of the invention.

Fig. 4 is a vertical cross sectional view of a preferred apparatus for forming a mist of a stabilized solution according to the present invention.

5 Figs. 5a and 5b show modifications of the apparatus of Fig. 4.

Fig. 6 is a schematic flow chart showing the preparation of a stabilized solution to be used in forming a thin film of lead zirconium titanate according to the present invention.

Detailed Description of The Invention

10 According to a primary aspect of the present invention, stabilized sources or stabilized solutions of desired chemical compounds will initially be prepared and then mists or vapors of the solutions will be generated, flowed into a deposition chamber and deposited in thin films/layers on substrates disposed within the deposition chamber. Such stabilized solutions include at least all of
15 those used in known liquid application techniques and specifically include sol-gels (which include alcohols as the solvent base thereof), metallorganic decomposition (MOD) formulations (which utilize n-decanoic acid as the solvent base thereof), solutions having water as the solvent base thereof, solutions having carboxylic acid as the solvent base thereof, etc.

20 The term "stabilized source" as used herein is intended to designate a source which is obtained by mixing precursors for each element using sol-gel techniques, or other wet chemistry mixing techniques, which lead to a common solvent, and then using the solution having that common solvent as the sole source for the entire compound. Other sources may also be used in parallel for
25 doping or modifying the compound. In the stabilized source the elements are already in the compound in solution with the common solvent or metallorganic precursor.

Use of the stabilized solutions is highly desirable for many reasons. First, the sources themselves are relatively easy to generate, even for complex
30 compounds. In this regard, there is an extensive amount of published literature available detailing various sol-gel preparation techniques, MOD formulation techniques, etc. used in relation to the known liquid application methods of

forming thin films, as discussed above. One such publication, Process Optimization and Characterization of Device Worthy Sol-gel Based PZT for Ferroelectric Memories is authored by two of the present inventors and others and appears in *FERROELECTRICS*, Vol. 109. The complete disclosure of the discussed publication is incorporated herein by reference thereto.

Further, the stabilized solutions used in the present invention are substantially less toxic and easier to handle than the corresponding reactants which are used in conventional, reactive CVD methods as discussed above, whereby the stabilized solutions can be handled and processed at substantially lower cost than the corresponding reactants.

Moreover, use of the stabilized compound sources assures high quality of the thin films produced thereby because the stabilized source can be accurately and consistently produced such that the desired chemical compound contained therein is uniformly, stoichiometrically correct, and because the deposition methods of the present invention do not involve any chemical reactions which might destabilize the chemical compound of its predetermined molecular formulation. Instead, thin films of the stabilized source are directly deposited on substrates from a mist/vapor under vacuum at ambient temperatures and subsequently dried.

Referring to Fig. 1, there is shown a thin film deposition apparatus according to a preferred embodiment of the invention, the apparatus being generally designated at 1. The apparatus 1 generally comprises a vacuum chamber 2, a substrate holder 4, a barrier plate 6, a nozzle assembly 8, and an exhaust assembly 10. The vacuum chamber 2 includes a main body 12, a lid 14 which is securable over the main body to define an enclosed space within the vacuum chamber, and the chamber is connected to an appropriate vacuum source (not shown) as generally indicated at 16. The lid 14 is preferably pivotally connected to the main body 12 using a hinge as indicated at 18.

The substrate holder 4 is preferably supported on a rotatable shaft 20 which is in turn connected to a motor (not shown) so that the holder may, if desired, be rotated during a deposition process. Indicated at 22 is an insulating connector which electrically insulates the substrate holder 4 and a substrate 5

supported thereon from the rest of the deposition apparatus 1 so that a DC or AC (RF) bias can be created between the substrate holder 4 and the barrier plate 6, if desired, utilizing the DC/RF feedthrough indicated at 23. Such a DC bias could be utilized, for example, for field-poling of thin films as they are being deposited on the substrate 5. For effecting such a DC bias an electrical source (not shown) would be operatively connected across the barrier 6 and the substrate holder 4.

The barrier plate 6 is preferably made of an electrically conductive material such as stainless steel, and is of sufficiently large size to extend completely over the substrate 5 in parallel thereto so that a vaporized source or mist as injected by the nozzle assembly 8 is forced to flow between the plate 6 and the substrate holder 4 over the substrate 5. As depicted, the barrier plate 6 is preferably connected to the lid 14 by a shaft 24 so that the plate 6 will be moved away from the substrate 5 whenever the lid is opened. The shaft 24 is preferably adjustable in length so that the spacing between the holder 4 and the plate 6 can be adjusted depending on the source materials, the flow rate, etc. For example, the spacing may be adjustable to define a spacing in the range of 2 - 50 mm.

The nozzle assembly 8 and the exhaust assembly 10 are more particularly shown with reference to Fig. 2. As depicted, the nozzle assembly 8 preferably includes an input tube 26 which receives a vaporized source from a manifold assembly 40 as discussed below in relation to Fig. 3, and an arcuate nozzle tube 28 having a plurality of small holes with removable screws 30 provided in a uniformly spaced manner along a surface of the tube 28 facing inwardly of the deposition chamber 2. The screws 30 can be selectively removed depending on the stabilized source, flow rate, etc. to adjust the flow of the vaporized source over the substrate 5. Indicated at 32 are end caps of the tube 28. The structure of the exhaust assembly 10 is substantially the same as that of the nozzle assembly 8, except that a pipe 34 leads to a vacuum/exhaust source (not shown). As depicted, the arcuate tube 28 of the nozzle assembly 8 and the corresponding arcuate tube of the exhaust assembly 10 will preferably surround respective, oppositely disposed peripheral portions of the substrate 5, and the arcuate tubes

will be spaced from each other across a central or intermediate portion of the substrate 5. Through such structure, and by adjusting the location of open holes in the two arcuate tubes, the flow of a vaporized source or mist over the substrate 5 can be well controlled for various sources, various flow rates, etc., for thereby achieving a uniform deposition of a thin film on the substrate 5.

Referring to Figs. 1 and 2, the substrate holder 4, the barrier plate 6, the nozzle assembly 8 and the exhaust assembly 5 collectively cooperate to define a relatively small deposition cavity surrounding an upper/exposed surface of the substrate 5, and within which the vaporized source is substantially contained throughout the deposition process.

Although preferred embodiments of the substrate holder, the barrier plate, the nozzle assembly and the exhaust assembly are shown and described, it will be understood that variations of such structures can be utilized within the scope of the present invention. For example, the arcuate nozzle and exhaust tubes could be replaced with tubes of other structures such as V-shaped or U-shaped, or could simply be replaced by a plurality of separate nozzles and separate exhaust ports.

Referring to Fig. 3, there is shown a manifold assembly 40 according to the present invention. The manifold assembly 40 is utilized for supplying a vaporized source to the nozzle assembly 8, and generally comprises a mixing chamber 42, a plurality of inlets 44 which are connected to corresponding source generators 46 through respective valves 48, a valve 50 for regulating flow from the mixing chamber 42 to the nozzle assembly 8, and an exhaust valve 52. In use, one or more of the source generators 46 are utilized to generate one or more different vaporized sources or mists which are then flowed into the mixing chamber 42 through the valves 48 and inlets 44. The vaporized sources as flowed into the mixing chamber 42 are mixed to form a single, uniform vaporized source or mist, which is then flowed into the vacuum chamber 2 at an appropriate flow rate through the valve 50. The valve 50 can be selectively closed off so that the vacuum chamber 2 can be pumped down to dry a deposited film of a stabilized liquid source, or to clean and purge the system when necessary. Similarly, the outlet of the exhaust valve 52 is connected to a

vacuum source (not shown) so that, when necessary to exhaust/purge one or more of the mist generators 46, the valve 50 can be closed off, the valve 52 and one or more of the valves 48 can be opened, and the mixing chamber 42 can be pumped down to clean and purge the source generator(s) and the mixing chamber.

It is preferred that a mist will be flowed from the manifold assembly 40 into the nozzle assembly 8 at ambient temperature or slightly above room temperature.

Referring to Fig. 4, there is shown a preferred source generator 46 according to the invention. The generator 46 includes a closed container 54, an ultrasonic transducer 56 fluid-tightly sealed into the bottom of the container 54, a valve 58 for introducing a stabilized liquid source such as a sol-gel or an MOD formulation into the container 54 while the container is maintained under sealed, vacuum-tight conditions, and an inlet port 60 and an outlet port 62 for passing a carrier gas through the container 54. In use, a stabilized liquid source 64 will be introduced into the container 54 through the valve 58 up to an appropriate level as measured by a level-detecting means (not shown), the transducer 56 is activated to generate a mist 66 of the stabilized liquid source, and an appropriate carrier gas is passed through the mist 66 via the ports 60, 62 where it becomes wet or saturated with the mist, and the wet carrier gas is then passed from the outlet port 62 into the manifold assembly 40 as discussed above. The carrier gas will normally be an inert gas such as argon or helium, but may comprise a reactive gas in appropriate situations. The valve 58 will be selectively actuated as necessary to maintain the stabilized liquid source 64 at an appropriate level within the container 54.

The preferred source generator 46 as shown in Fig. 4 is particularly advantageous because it creates a vaporized source which can be effectively flowed or injected into the vacuum deposition chamber 2 without complications such as freezing.

Referring to Fig. 5a there is shown a source generator 46' which is a modification of the source generator 46 shown in Fig. 4 whereby the ultrasonic transducer 56 does not come into contact with the stabilized liquid source 64.

Instead, the stabilized liquid source 64 is contained within a first, closed container 54' while the transducer 56 is sealingly fitted to a bottom wall of a second, open container 68, a working medium 70 such as water or another liquid is disposed in the second container 68 over the transducer, and the first container 54' is disposed in spaced relation above an upper surface of the working medium 70 such that a mist plume 72 of the working medium created by the ultrasonic transducer contacts a bottom wall of the first container 54' for thereby creating the mist 66 of the stabilized liquid 64 within the first container 54', which is then flowed into the manifold assembly 40 in the same manner as discussed above in relation to Fig. 4. The modified source generator 46' shown in Fig. 5 has all of the advantages of the source generator 46 shown in Fig. 4, as well as an additional advantage that the ultrasonic transducer 56 does not become contaminated with a stabilized liquid used to form a desired thin film.

Referring to Fig. 5b there is shown another modification of the mist generating apparatus of Fig. 4. The modification of Fig. 5b is very similar to that of Fig. 4 except that the transducer 56 is suspended in the generator 46'' above the stabilized liquid source rather than being sealed into the bottom wall of the container.

Although the source generators 46, 46', 46'' shown in Figs. 4, 5a and 5b are preferred according to the invention, it will be understood that other source generators could be utilized according to the invention. For example, a stabilized liquid source could be provided within a closed container and an appropriate carrier gas could be simply bubbled through the stabilized liquid and then flowed into the mixing chamber 40; or a spray nozzle could be used to generate a mist of a stabilized liquid source within a closed container, and an appropriate carrier gas could be flowed through the mist and into the mixing chamber 40 using an inlet and outlet port similar to the ports 60, 62 shown in Fig. 4.

An example of the sol-gel synthesis of YMnO_3 follows. 1 gm. of yttrium isopropoxide $\text{Y}[\text{OCH}(\text{CH}_3)_2]_3$ was mixed with 8 ml. of 2-methoxyethanol. The yttrium isopropoxide did not go into solution, but was forced into solution by the addition of approximately 25 drops (slightly over one ml.) of hydrochloric acid.

0.25 grams of manganese acetate $\text{Mn}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ was mixed with 5 ml. 2-methoxyethanol. The manganese acetate would not dissolve in the 2-methoxyethanol, but was forced into solution by the addition of approximately 10 drops of hydrochloric acid.

5 The yttrium and manganese solutions were then mixed together at room temperature resulting in a slightly yellow colored solution. The resulting YMnO_3 solution did not form a film when spun onto a silicon wafer. Adding H_2O for hydrolysis did not improve the film-forming characteristics. However, the addition of approximately 25 drops of titanium isopropoxide (a gel former) to
10 the yttrium/manganese solution resulted in a solution which remained clear for approximately 3 hours and formed good films when spun onto a silicon wafer.

Referring to Fig. 6, there is shown an exemplary flow chart depicting the preparation of a stabilized liquid solution of lead zirconium titanate (PZT hereinafter) to be deposited utilizing the apparatus of Figs. 1-5. At steps P_1 - P_3 ,
15 stabilized liquid precursors of titanium isopropoxide, zirconium N-propoxide and lead acetate are respectively formed utilizing 2-methoxyethanol as the common solvent of each of the precursors. At step P_4 the stabilized solutions of titanium isopropoxide and zirconium n-propoxide are mixed, while at step P_5 such mixture is further mixed with the stabilized solution of lead acetate precursor together
20 with dopants or additives (if any) desired in the thin film to be deposited. At step P_6 the final mixture of P_5 is filtered to form a stock solution as shown in P_7 . Table I below presents a more detailed analysis of steps P_1 - P_7 .

TABLE I

SOL-GEL PZT SOLUTION PROCESS FLOW SHEET

- 100 **STOICHIOMETRY**
- 110 Pb: $94.7 \text{ gm Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O} = 0.25 \text{ moles Pb.}$
- 5 120 Zr: $46.8 \text{ gm Zr n-propoxide}(30\% \text{ propanol by weight}) = 0.10 \text{ moles Zr.}$
- 130 Ti: $42.6 \text{ gm Ti-isopropoxide} = 0.15 \text{ moles Ti.}$
- 140 10:1 mole ratio (moles 2-methoxyethanol:moles metal).
- 200 **LEAD PRECURSOR**
- 10 210 $94.73 \text{ gm Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ is added to 197 ml 2-methoxyethanol.
- 220 Distill solution to a final vapor temperature of 114°C.
- 230 Amount of final distillate: 107 ml.
- 300 **ZIRCONIUM PRECURSOR**
- 15 310 $46.82 \text{ gm Zr n-propoxide}$ in propanol is added to 79 ml 2-methoxyethanol.
- 320 Distill solution to a final vapor temperature of 113°C.
- 330 Amount of final distillate: 79 ml.
- 400 **TITANIUM PRECURSOR**
- 410 $42.62 \text{ gm Ti-isopropoxide}$ is added to 118 ml 2-methoxyethanol.
- 20 420 Distill solution to a final vapor temperature of 114°C.
- 430 Amount of final distillate: 76 ml.
- 500 **MIXING OF PRECURSORS**
- 510 Add Ti precursor to Zr precursor and stir.
- 520 Add TiZr solution to Pb solution and stir for $\frac{1}{2}$ hour(s).
- 25 530 Amount of PZT stock solution: 250 ml.
- 540 Filter PZT stock solution through an appropriate size syringe filter.
- 550 Molarity of solution: 1.0 M (moles PZT/l of solution).

At step P_8 the stock solution of P_7 is hydrolyzed using acetic acid and H_2O or other appropriate materials, although such hydrolyzation step may be omitted as indicated by the dotted line extending from P_7 to P_9 . The steps P_1 through P_8 are conventional steps utilized in forming sol-gels used in conventional spin-on thin film forming procedures.

At step P_9 , the conventional stock solution of P_7 or the conventional hydrolyzed solution of P_8 are modified for use in the deposition processes of the present invention.

Such step P_9 essentially involves adjusting the concentration of the desired chemical compound in the sol-gel, or other stabilized liquid source, such that small droplets of the vaporized source (mist) as flowed into the vacuum chamber 2 will deposit onto the substrate 5, spread out and interconnect to form a uniform film of the sol-gel over the entire upper surface of the substrate 5. In other words, the sol-gel concentration will be adjusted such that a film of the sol-gel will deposit completely over the substrate 5 before a significant amount of drying of the individual droplets occur, which would undesirably result in the creation of small disconnected particles on the substrate, the particles ultimately resulting in a thin film which is very porous and/or granular. Determination of the appropriate concentration of chemical compound in the sol-gel or other stabilized liquid source involves considerations of the particular chemical compound and solvent used in the stabilized liquid source, as well as of the vacuum level maintained within the vacuum chamber 2. For example, solvents having relatively high boiling points, such as 2-methoxyethanol used in the PZT sol-gel discussed above, are slower to dry than solvents having relatively low

boiling points such as methanol; while higher vacuum levels result in faster drying of any given stabilized liquid source.

With the deposition of PZT from a sol-gel as prepared in the manner discussed above, and with the vacuum chamber 2 operating at a vacuum of 5 570-575 Torr, it is preferred that the stock solution of P_7 or the hydrolyzed solution of P_8 will be modified in step P_9 by the addition of 10-15 percent (by volume) of methanol. In other words, the normal sol-gel is diluted to a sufficient degree to assure that the small droplets of the vaporized source which deposit on the substrate 5 are sufficiently fluid to spread out and interconnect to form 10 a continuous, uniform film as discussed above.

Although methanol is the preferred diluent for the sol-gel of PZT according to the present invention, it will be understood that other diluents (including 2-methoxyethanol) could be used for diluting the sol-gel of PZT, and that various other diluents would be utilized with other sol-gels and with other 15 stabilized liquid sources used according to the present invention.

At step P_{10} the modified solution of step P_9 is vaporized using a source generator such as shown in Figs. 4 or 5, and is flowed into the deposition apparatus 1 through the manifold assembly 40 where it is deposited on the substrate 5 to form a thin film of the sol-gel. The thickness of the deposited thin 20 film will be continuously monitored by conventional means (not shown).

At drying step P_{11} the substrate 5 having a thin film of the sol-gel or other stabilized liquid source thereon is subjected to vacuum to remove the solvent from the sol-gel, thus leaving a thin film of the desired chemical compound on the substrate, while at step P_{12} the thin film of the chemical compound will, if

necessary, be annealed. In drying step P_{11} , drying of the sol-gel film may alternatively be accomplished by using a heating means to bake or otherwise heat the deposited film. Further, with many complex thin films, such as ferroelectrics, it is necessary to activate the dried thin film by annealing before
5 the films will function in a desired manner. The drying and annealing steps P_{11} , P_{12} may be effected within the vacuum chamber 2 using appropriate heating means or may be performed in different apparatus outside of the vacuum chamber 2.

At step P_{13} the substrate having a thin film of the chemical compound
10 thereon is further processed, such as by having a top electrode deposited thereon. The apparatus of the first embodiment of the present invention, as discussed above in relation to Figs. 1-5 is very advantageous because it effectively combines the best of vacuum, CVD, and wet chemistry (sol-gel, MOD, etc.) techniques to readily produce very complex, multi-element films in a controlled
15 environment. Some specific advantages include the ability to carefully, consistently control the stoichiometry of thin films being deposited, the relative ease with which stabilized liquid sources may be generated and handled, the ability to keep the deposited films free from contaminants (because the deposition process is operated under vacuum conditions), the ability to form very
20 thin, uniform films fully covering a substrate surface, etc.

As indicated by the structure of the deposition apparatus 1 shown in Fig. 1, i.e., the lack of any heating means therein, it is preferred that the deposition process according to the invention will be conducted at room/ambient temperatures.

As discussed above in relation to Figs. 4 and 5, an aspect of the invention is that the stabilized compound sources are agitated ultrasonically to atomize the sources before they are introduced into the process chamber. Depending upon the particular stabilized source and application, it may be desirable to heat the
5 lines through which the vapor is introduced into the manifold assembly and/or into the process chamber.

Another aspect of the invention involves a solvent exchange technique. Many times a compound X will dissolve in one particular solvent only and no other solvent. Similarly, a compound Y may dissolve in a different solvent and
10 the solvent for compound X is not compatible with the solvent for compound Y. With the present invention, a solvent exchange technique arrives at a common solvent in order to produce a sol-gel or other stabilized liquid having compounds X and Y.

The invention is advantageous in depositing complex, compound thin films
15 of materials such as ferroelectrics, super-conductors, materials with high dielectric constants, gems, etc., but is not limited to depositing such complex thin films.

Although there has been described what is at present considered to be the preferred embodiment of the present invention, it will be understood that
20 the invention can be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment is, therefore, to be considered in all aspects as illustrative and not restrictive. The scope of the invention is indicated by the appended claims rather than the foregoing description.

WE CLAIM:

1 1. A method of forming a thin film of a chemical compound on a
2 substrate, comprising the steps of:
3 forming at least one stabilized solution of a chemical compound and a
4 solvent;
5 providing a substrate within an enclosed deposition chamber;
6 producing a mist of said stabilized solution; and
7 flowing the mist into the deposition chamber such that the mist deposits
8 and forms a film of the stabilized solution on an exposed surface of the
9 substrate.

1 2. A method according to claim 1, including a further step of drying said
2 deposited film of the stabilized solution to remove the solvent therefrom.

1 3. A method according to claim 1, wherein said deposition chamber is
2 maintained at substantially ambient temperature and under vacuum and said
3 mist is flowed into said deposition chamber at substantially ambient temperature.

1 4. A method according to claim 1, wherein said mist as flowed into the
2 deposition chamber is contained within a small cavity surrounding said exposed
3 surface of said substrate.

1 5. A method according to claim 1, wherein said mist is flowed into said
2 deposition chamber from a plurality of ports disposed in close proximity around
3 one peripheral portion of said substrate, and said mist is drawn off by a plurality
4 of exhaust ports disposed in close proximity around another peripheral portion
5 of said substrate opposite to said one peripheral portion.

1 6. A method according to claim 3, wherein a concentration of said
2 chemical compound in said stabilized solution is controlled in dependence on the
3 temperature and the vacuum level within said deposition chamber such that mist
4 droplets of said stabilized solution which deposit on said substrate spread out
5 and interconnect to form a uniform film.

1 7. Apparatus for depositing a thin film on a substrate, comprising:
2 a deposition chamber having an enclosed space therein;
3 means for supporting a substrate within said deposition chamber;
4 means for producing a mist of a stabilized solution of a chemical
5 compound; and
6 means for flowing said mist into said deposition chamber such that the
7 mist deposits and forms a thin film of the stabilized solution on said substrate.

1 8. Apparatus according to claim 7, including means for maintaining said
2 deposition chamber under vacuum.

1 9. Apparatus according to claim 7, including means for containing a mist
2 as flowed into the deposition chamber within a small portion of the enclosed
3 space inside the deposition chamber surrounding an exposed surface of said
4 substrate.

1 10. Apparatus according to claim 9, wherein said containing means
2 includes a substrate holder supporting said substrate thereon and a barrier plate
3 disposed in spaced relation above said substrate holder in parallel thereto.

1 11. Apparatus according to claim 10, wherein said containing means
2 further includes a nozzle assembly disposed in close proximity around one
3 peripheral portion of said substrate and an exhaust assembly disposed in close
4 proximity around another peripheral portion of said substrate opposite to said
5 one peripheral portion.

1 12. Apparatus according to claim 7, including means for rotating said
2 substrate during a deposition process; and

3 said mist flowing means includes a plurality of nozzle ports disposed
4 around one peripheral portion of said substrate and adapted to flow said mist
5 in parallel over said exposed surface of said substrate.

1 13. Apparatus according to claim 12, including means for exhausting mist
2 after it is flowed over said substrate, said exhausting means including a plurality
3 of exhaust ports disposed in close proximity around another peripheral portion
4 of said substrate opposite to said one peripheral portion of said substrate.

AMENDED CLAIMS

[received by the International Bureau on 14 August 1992 (14.08.92);
new claim 14 added; original claims 1,2,4-12 amended; remaining claims
unchanged (4 pages)]

1 1. A method of forming a thin film of a chemical compound on a substrate,
2 comprising the steps of:

3 forming at least one stabilized metalorganic solution of a desired chemical compound
4 and a solvent, said solution containing a substantially stoichiometrically-correct quantity of
5 said chemical compound;

6 providing a substrate within an enclosed deposition chamber;

7 producing a mist of said stabilized solution;

8 flowing the mist into the deposition chamber such that the mist deposits and forms
9 a thin uniform film of the stabilized solution on an exposed surface of the substrate; and

10 drying the thin film of said stabilized solution to remove organic matter therefrom.

1 2. A method according to claim 1, including a further step of maintaining an
2 electrical bias within a small portion of said enclosed space surrounding said exposed surface
3 of said substrate.

1 3. A method according to claim 1, wherein said deposition chamber is maintained
2 at substantially ambient temperature and under vacuum during the mist flowing step and
3 said mist is flowed into said deposition chamber at substantially ambient temperature.

1 4. A method according to claim 3, wherein a concentration of said chemical
2 compound in said stabilized metalorganic solution is controlled in dependence on the
3 temperature and the vacuum level within said deposition chamber such that mist droplets
4 of said stabilized solution which deposit on said substrate spread out and interconnect to
5 form said uniform thin film.

1
2 5. A method according to claim 1, wherein said mist is flowed into said deposition
3 chamber from a plurality of ports disposed in close proximity around one peripheral portion
4 of said substrate, and said mist is drawn off by a plurality of exhaust ports disposed in close
5 proximity around another peripheral portion of said substrate opposite to said one
6 peripheral portion; and

7 said method includes further steps of supporting said substrate on a rotatable holder
8 and providing a barrier plate in narrowly spaced relation parallel to said exposed surface of
9 said substrate such that said barrier plate, said holder, said nozzle assembly and said exhaust
10 assembly define a small cavity surrounding said exposed surface of said substrate.

1 6. A method according to claim 1, including a further step of containing said mist
2 as flowed into the deposition chamber within a small cavity surrounding said exposed surface
3 of said substrate.

1 7. Apparatus for depositing a thin film of a chemical compound on a substrate,
2 comprising:

3 a deposition chamber having an enclosed space therein;

4 means for supporting a substrate within said deposition chamber;

5 means for producing a mist of a stabilized metalorganic solution containing a
6 substantially stoichiometrically-correct quantity of a desired chemical compound;

7 means for flowing said mist into said deposition chamber such that the mist deposits
8 and forms a thin uniform film of the stabilized solution on an exposed surface of said
9 substrate; and

10 means for drying said thin film of said stabilized solution to remove organic matter
11 therefrom.

1 8. Apparatus according to claim 7, including means for maintaining said
2 deposition chamber under vacuum and means for maintaining the deposition chamber at
3 substantially ambient temperature when the mist is being flowed therein.

1 9. Apparatus according to claim 7, including means for containing a mist as
2 flowed into the deposition chamber within a small portion of the enclosed space inside the
3 deposition chamber surrounding said exposed surface of said substrate.

1 10. Apparatus according to claim 9, wherein said containing means includes a
2 substrate holder supporting said substrate on one surface of the holder and a barrier plate
3 disposed in a narrowly spaced relation parallel to said substrate holder and facing said
4 substrate.

1 11. Apparatus according to claim 10, wherein said containing means further
2 includes a nozzle assembly disposed in close proximity around one peripheral portion of said
3 substrate and an exhaust assembly disposed in close proximity around another peripheral
4 portion of said substrate opposite to said one peripheral portion, said substrate holder, said
5 barrier plate, said nozzle assembly and said exhaust assembly collectively defining said small
6 portion of said enclosed space.

1 12. Apparatus according to claim 7, including means for rotating said substrate
2 during a deposition process;

3 said mist flowing means includes a plurality of nozzle ports disposed around one
4 peripheral portion of said substrate and adapted to flow said mist in parallel over said
5 exposed surface of said substrate; and

6 a barrier plate disposed in narrowly spaced relation parallel to said exposed surface
7 of said substrate to define a narrow gap therebetween.

1 13. Apparatus according to claim 12, including means for exhausting said mist after
2 it is flowed over said substrate, said exhausting means including a plurality of exhaust ports
3 disposed in close proximity around another peripheral portion of said substrate opposite to
4 said one peripheral portion of said substrate.

1 14. Apparatus according to claim 7, including means for maintaining an electrical
2 bias within a small portion of said enclosed space surrounding said exposed surface of said
3 substrate.

STATEMENT UNDER ARTICLE 19

Independent claims 1 and 7 have been amended to define that the stabilized solution is a metalorganic solution containing a substantially stoichiometrically-correct quantity of a desired compound, that the mist of the solution forms a thin uniform film on an exposed surface of the substrate and that the film or solution is dried to remove organic matter therefrom.

Claim 2 and new claim 14 define a step/means for maintaining an electrical bias in a small space surrounding the substrate.

Claim 5 is amended to further define the rotatable substrate holder, the barrier plate, and the cavity defined by the holder, the barrier plate, and the nozzle and exhaust assemblies.

Claim 8 is amended to define means for maintaining the deposition chamber and substantially ambient temperature; claim 12 is amended to define the barrier plate; the number of claims 4 and 6 has been reversed such that original claim 4 is now claim 6 and vice versa; and the language of claims 4, 6, 9 and 10 has been slightly amended to overcome minor informalities.

Claim 11 is amended to define the collective function of the substrate holder, the barrier plate, nozzle assembly in the exhaust assembly collectively define the small portion of the enclosed space.

All of the claim amendments are fully supported in the disclosure of the originally filed application.

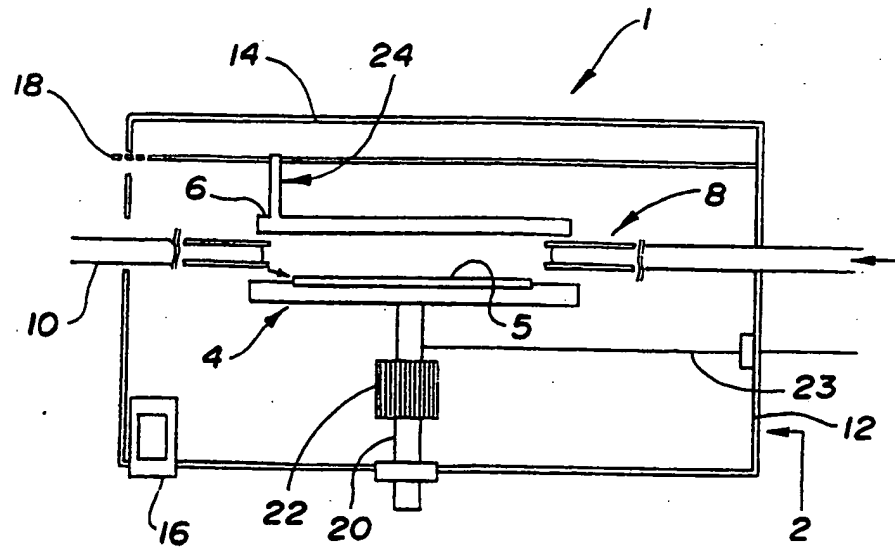


Fig. 1

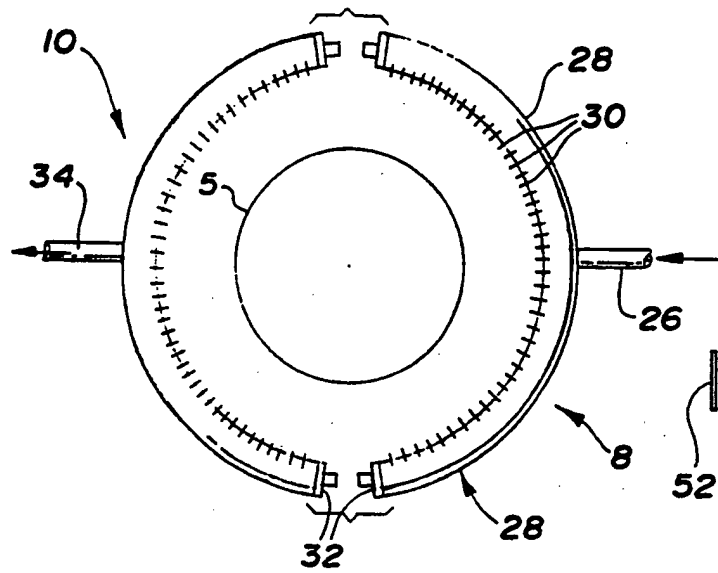


Fig. 2

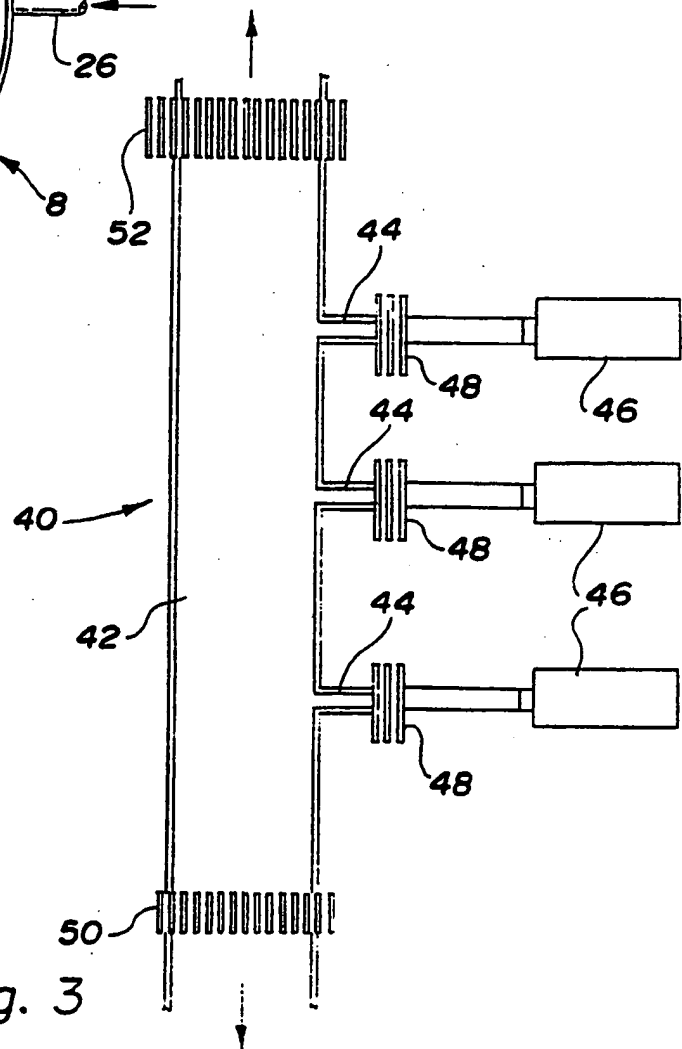
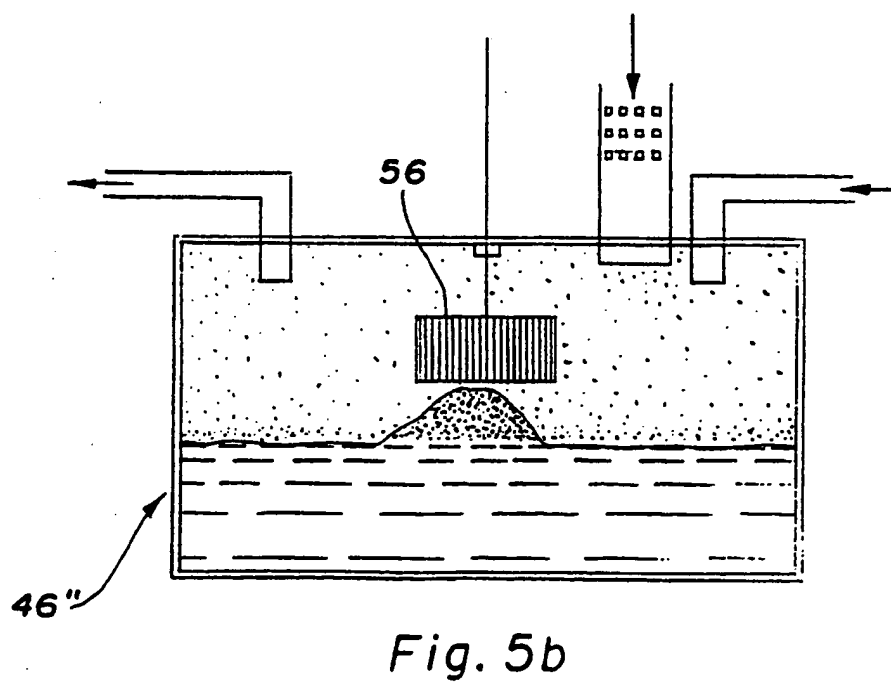
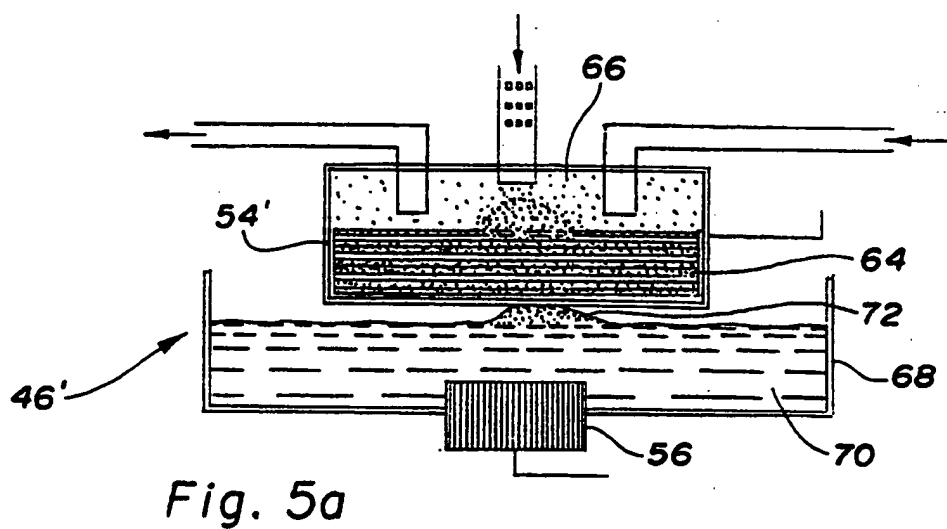
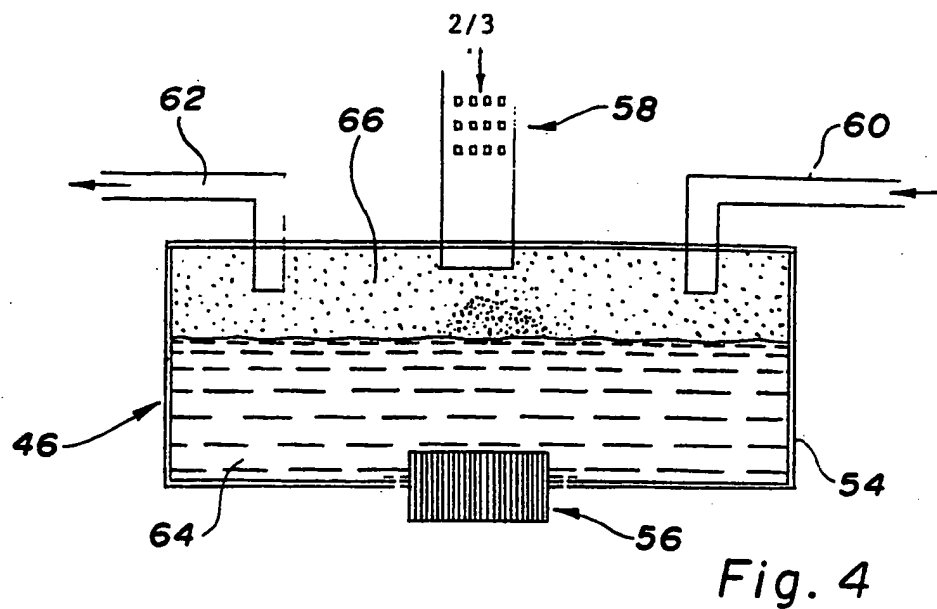


Fig. 3



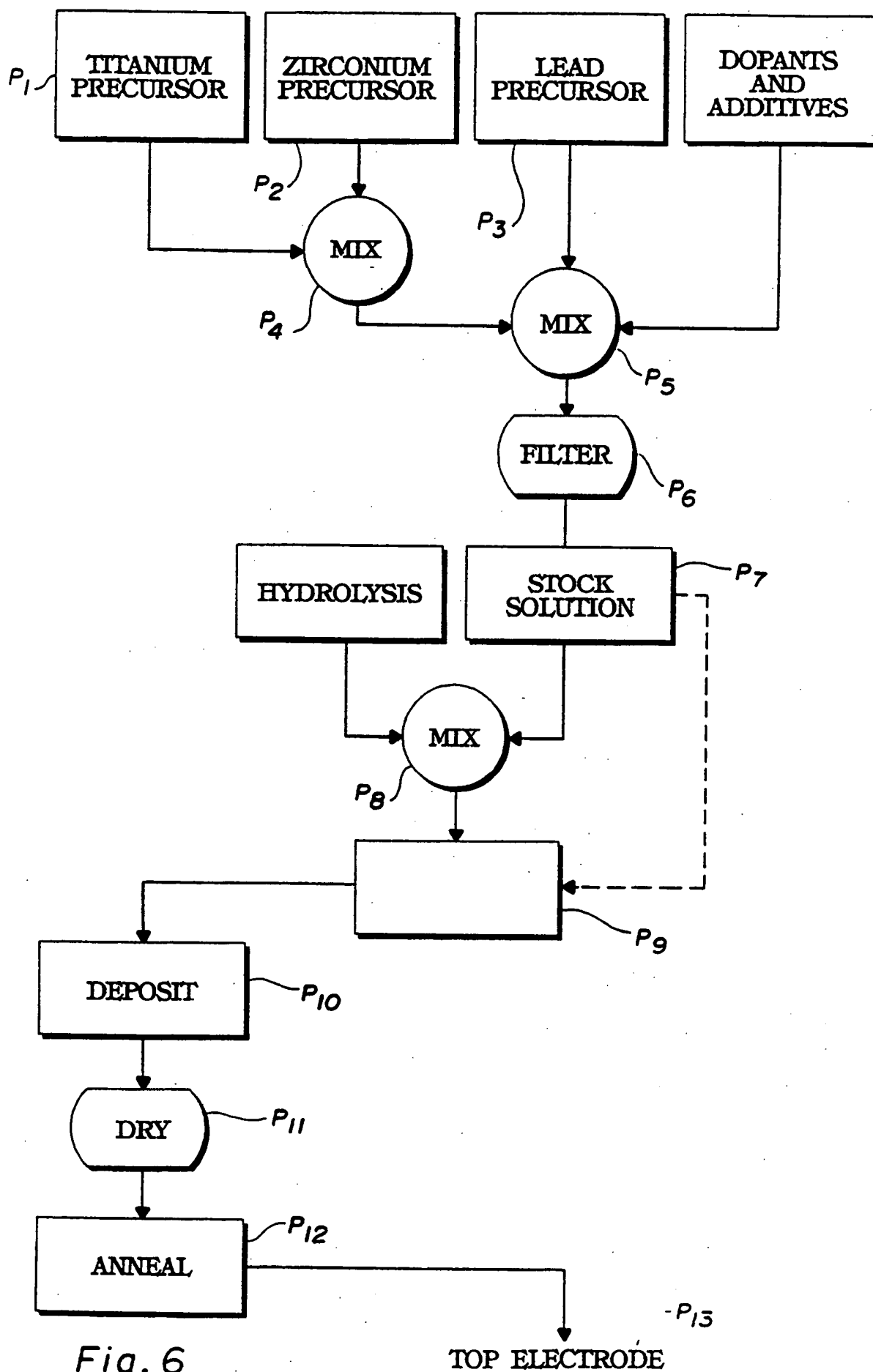


Fig. 6

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5) HO1L 21/00

US 118/50.1, 314

US 427/251,250.2

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System

Classification Symbols

US

118/715,50,50.1,323,314
427/421,424,250,251,255.1,255.2

Documentation Searched other than Minimum Documentation
to the extent that such documents are included in the fields searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No. 1
X	US; A; 4290384; Ausschnitt et. al.; 22 September 1981; figure 1; columns 1-5	1-2,7
A	US; A; 4508054; Boumferger et. al.; 02 April 1985; figure 1; columns 3-4	1-13
<u>X</u> <u>Y</u>	US; A; 5041229; Brock et. al.; 20 August 1991; figure 1; columns 1-10	<u>7-8</u> <u>1-3</u>
X	US; A; 4689247; Doty et. al.; 25 August 1987; figures 1-2; columns 6-7	1-4,7,9-10
A	US; A; 3473959; Ehinger et. al.; 02 August 1965; figure 1; column 2-5	7-13
X	US; A; 5069157; Imai et. al.; 03 December 1991; figure 5; columns 1-5	1-2,4-5,7, 9-13

*** Special categories of cited documents:**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claims or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

7* prior document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

8* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

9* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

* "A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Making of the International Search Report

19 MAY 1992

17 JUN 1992

International Searching Authority

Signature of Authorized Officer

ISA/US

Goerge Goudreau

A	US; A; 4650539; Irvine et. al., 17 March 1989; figure 1; columns 2-5	1-13
X	US; A; 3880112; Spitz et. al.; 29 April 1975; figure 1; columns 1-6	1-2,7
X	US; A; 4783006; Hayashi et. al., 08 November 1988, figures 2-3, columns 1-5	1-2,4,7,9

☒ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1 ☐ Claim numbers _____ because they relate to subject matter not required to be searched by this Authority, namely:

2 ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out is, specifically:

3 ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(c).

☐ **VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING**

This International Searching Authority found multiple inventions in the international application as follows:

1 ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2 ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3 ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4 ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority does not require payment of any additional fee.

Remarks on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.